A SOLVENT FREE METHOD FOR DEOXIMATION REACTION

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ABSTRACT

Oxime is an important intermediate for protection, purification and characterization of carbonyl compounds. Various mathods are adopted for deoimation process to obtain the parent carbonyl. A simple procedure for deoximation in solvent free condition is reported using modified clay as catalyst. Under the conditions developed in this effort, various ketones and aldehydes are produced in good to excellent yields.

General Reaction
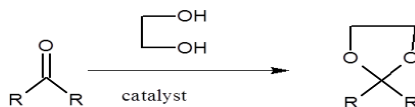
Where R = H, aromatic, aliphatic

KEYWORDS: Deoximation, Solvent Free Condition, Heteropoly Acids, Bentonite

INTRODUCTION

Protection of carbonyl group as oximes is of great importance in organic synthesis. Oximes are readily prepared and highly stable compounds [1]. Oximes are extensively used for purification and characterization of carbonyl compounds [2,3] and as intermediates for many reactions such as the preparation of amides by Beckmann rearrangement [4] . Oximes can also be prepared from non-carbonyl compounds therefore, generation of carbonyl compounds from oximes provide an alternative for the synthesis of aldehydes and ketones [5]. The cleavage of oximes to regenerate the parent carbonyl compounds is an important synthetic process as oximes are employed as aldehyde and ketone functional group equivalent in organic synthesis.

So far a good number of deoximation methods based on hydrolytic [6], reductive [7–10], oxidative [11–17], and transoximation [18–20] reactions have been developed. But most of them require strong acidic conditions, take long reaction times, and give low product yields, while some are performed at higher temperatures. For example, regeneration of carbonyl compounds from oximes via direct hydrolysis usually involves strong acidic conditions due to the relatively high hydrolytic stability of oximes, and thus leads to the damage of acid-sensitive groups and the formation of amides as byproducts by Beckmann rearrangement [21,22]. Besides, most of reductive and oxidative methods require reagents that are often hazardous or very toxic, expensive or not readily available.

Several metallic and non-metallic deoximation reagents such as tert-butylhydroperoxide [23], trimethyl ammonium chlorochromate [24], pyridinium chlorochromate-H_2O_2 [25], thallium nitrate [26], $KMnO_4$/alumina[27],N,Ndibromo-N,N-1,3-propylene-bis[(4methylphenyl)]sulphonamide [28], metalloporphyrins [11], N-bromosuccinimide [29], surfactant/I_2/water [15], chloranil [30], ammonium persulfate [31], platinum(II) terpyridyl acetylide complex [32], $NaHSO_4H_2O$-supported CrO_3 [33], periodic acid [34], ferric nitrate [35] etc. have been developed

over the years. Very recently, conversion of oximes to the carbonyl compounds has been demonstrated with use of 2-nitro-4,5-dichloropyridazin-3(2H)-one under microwave irradiated conditions [36]. However, the main drawbacks associated with these systems are harmful and expensive metals, long reaction time, toxic organic solvents, and in majority of cases they require an elevated temperature. Thus development of deoximation systems which are readilyaccessible, air/moisture stable, inexpensive, environmentally acceptable, that can promote deoximation under mild reaction conditions are still desirable.

Therefore a milder, non-hazardous and inexpensive selective reagent is very much in demand. Heteropoly acids due to their unique physicochemical properties can be profitably used in homogeneous, biphasic or heterogeneous systems providing a broad operational choice. The high effectiveness of HPAs as acid catalysts is primarily due to their strong Bronsted acidity greatly exceeding (100-1000 times) than that of ordinary mineral acids.

But there are certain limitations associated with the use of HPAs as they have low surface area and thermal stability with no reusability which can be overcome by the use of clay possessing a higher surface area, porosity and efficient reusability. But the acidic strength of natural clay is lower than that of mineral acids that can be further be enhanced by using heteropoly acid intercalated clay. HPAs can be intercalated into clay thereby leading to a catalyst possessing a higher surface area, acidic strength, porosity and efficient reusability.HPA intercalated clay catalyst thus could prove to be a green catalyst for replacement of conventional acid catalyst used in various organic synthesis.

EXPERIMENTAL

Catalyst Preparation

Na-Bentonite

1.0 g of Bentonite clay was added into a 250 ml conical flask containing 50 ml of 1.0 M NaCl this clay suspension was stirred for 16 hours. The residue after centrifugation was washed several times with double distilled water till complete removal of chloride ions. The residue thus obtained after above procedure was dried in an oven at 100°C to generate the Na form of the Bentonite (Na-Ben).

Al-Pillared Bentonite (Al-Ben)

In a 250 ml conical flask containing 1.0 g of Na-Ben, in 100 ml of double distilled water, 50 ml of the pillaring solution (keggin ion) was gradually added with vigorous stirring for 16 hours. The residue was washed several times with double distilled water till the complete removal of chloride ions was confirmed by $AgNO_3$ test. The residue, thus obtained was dried in an oven at 100°C is referred to as Al-Pillared Bentonite (Al-Ben) [37].

Acid Activated Bentonite (H^+-Ben)

5.0 g of Na-Ben was added into a 100 ml beaker containing 50 ml of 3N H_2SO_4, this mixture was exposed to microwave radiation for 30 minutes. The residue was washed several times with double distilled water till the complete removal of SO_4^{2-} ions was confirmed by $BaCl_2$ test. The residue thus obtained was dried in an oven at 100°C to generate the Acid activated Bentonite (H^+-Ben) [39].

Pillared Acid Activated Bentonite (Paa-Ben)

1.0 g of H^+ Ben, was added into a 250 ml conical flask containing100 ml of double distilled water. 50ml of pillaring solution was gradually added with vigorous stirring for 16 hours. The residue was washed several times with double distilled water till the complete removal of chloride ions was confirmed by $AgNO_3$ test. The residue thus obtained was dried in an oven at 100°C and is referred to as Pillared Acid Activated Bentonite (PAA-Ben).

Phosphomolybdic Intercalated Bentonite (PMA –Ben)

In a 250 ml round bottom flask, 1.0 g Na-Ben was suspended in 50 ml double distilled water. To this, aqueous solution of Phosphomolybdic acid (100mg) was added drop wise and then stirred for 16 hrs. After this, the mixture was filtered and washed with double distilled water to remove the excess of Phosphomolybdic acid. The product was dried at 100^0C.

General Procedure for Deoximation

In order to elucidate the role of the PMA-Ben as catalyst, a controlled reaction was carried out using PMA, bentonite, Al-Ben, H^+-Ben, PAA-Ben and PMA-Ben as catalyst with benzaldehyde oxime as reactant. The best results were obtained with PMA-Ben in microwave.

A number of aromatic aldehyde & ketone oximes (10 mmol) were mixed with the PMA-Ben (50 mg). The mixture was exposed tomicrowave irradiation. After irradiation of the mixture for a specified time period, the content was gradually cooled to room temperature. The efficiency of each reaction was monitored by TLC. After confirming the completion of the reaction, the catalyst was recovered by filtration. The catalyst thus separated by filtration was washed several times with absolute ethanol to remove organic matter. The residue obtained after evaporation of the solvent from the filtrate was purified using TLC/column chromatography with $CHCl_3$:MeOH with increasing polarity.

Optimization of Reaction Conditions

For the optimization of reaction conditions 10 mmol of Benzaldehyde oxime have been selected as reactants.

Optimization of the Catalysts Amount

Reactions have been performed using varying amount of different catalysts under uniform conditions. Table 1.

Optimization of Time

The reaction time has been optimized by performing reactions at regular intervals of time. After a certain time period there is not much increase in the yield. That time has been selected as optimum time. Table 2.

After optimization of time and amount of catalyst a number of acetal derivatives have been synthesized table 3.

RESULTS AND DISCUSSIONS

Catalyst Characterization

X-Ray Diffraction

The XRD pattern of Ben [39], Na-Ben and H^+-Ben show a sharp peak at 2θ = 5.93, 6.83 and 9.67 respectively corresponding to a d-value of 14.9 Å, 12.9 Å and 9.1 Å. A decrease in the d-value of 2 Å and 5.8 Å is observed when interlayer cations (Ca^{+2}) are replaced by the smaller ions, Na^+ and H^+ respectively.PAA-Ben, shows a further shift in the peak position, 2θ =5.30 and a d-value of 16.6 Å corresponding to an increase in the interlayer region by 7.5 Å w.r.t H^+-Ben confirms the intercalation of Al Keggin ion into the interlayer region of H^+-Ben. The Al-Ben shows a peak at 2θ = 5.20 and a d-value of 16.9 Å corresponding to an increase in the d-value of 4 Å w.r.t Na-Ben thus confirming the intercalation of Al Keggin ion in the interlayer region of Na-Ben. PMA-Ben, show a peak at 2θ = 5.44 corresponding to a d-value of 16.2Å. This increase in the d-value 3.3 Å w.r.t Na-Ben confirms the intercalation of PMA in the interlayer region of Na-Ben.

Total Surface Area

Total surface area studies have been performed by EGME method. Surface area values of Ben, Na-Ben, H^+-Ben,

Al-Ben, PAA-Ben, STA-Ben are represented in the Table 1.4. Total surface area of Ben has been found to be 215 m^2/g. After conversion to Na-Ben total surface area has been found to be 121 m^2/g which may be due to the decrease in d-spacing as indicated by XRD data. Total surface area of H^+- Ben has been found to be 327 m^2/g. Although Na ions are replaced by H^+ ions, but acid activation also causes the formation of small pores, consequently increasing the surface area [40,41]. Total surface area of Al-Ben has been found to be 295 m^2/g. Due to the intercalation of Al-Keggin ion the inner surface also becomes assessable. PAA-Benhas been found to have a total surface area of 350 m^2/g which is again due to intercalation of Al-Keggin ion in H^+-Ben. Total surface area of PMA-Ben has been found to be 296 m^2/g further confirming the intercalation of PMA.

Thermal Method of Analysis

The thermogram (TGA) of Ben, Na-Ben, H^+-Ben (Figure 4) shows four step weight loss pattern. The first step, up to 180^0C, corresponds to dehydration of surface adsorbed water. The second step, 180^0C to 550^0C, is attributed to dehydration of interlayer water. The third step 550^0C to 675^0C, is attributed to the gradual dehydroxylation of clay layers. Beyond 675^0C the clay loses its structure and practically shows no weight loss [42].

The TGA of PAA-Ben, Al-Ben (Figure 5) shows a similar four step weight loss pattern. The first step, up to 200^0C, corresponds to dehydration of surface adsorbed water. The second step, 200^0C to 350^0C, is attributed to dehydration of interlayer water. The third step, 350^0C to 600^0C, is attributed to the gradual dehydroxylation of clay layers. Beyond 600^0C the clay loses its structure and practically shows no weight loss [42].

The TGA of PMA-Ben (Figure 6) shows four step weight loss pattern, the first step, up to 150^0C, corresponds to dehydration of surface water. The second step, 150^0C to 350^0C, is attributed to dehydration of interlayer water. The third step, 350^0C to 550^0C, is attributed to the dehydroxylation of clay layers and the loss of keggin ion structure.

Fourier Transform Infrared Analysis

Vibrational spectra of Ben, Na-Ben, H^+-Ben, Al-Ben and PAA-Ben clays (Figure 1 and 2) indicate two strong absorption bands ~3626 cm^{-1} and ~3436 cm^{-1} corresponding to the stretching vibrations of the O-H group originating from the surface adsorbed and interlayer water. The ~1642 cm^{-1} band in these samples has been assigned to the H–O–H bending vibrations of water. The ~1043 cm^{-1} and ~796 cm^{-1} bands are attributed to the stretching vibration of the Si-O bond. The ~522 cm^{-1} and ~466 cm^{-1} bands have been assigned to the Si–O–Al and Si–O–Si deformation vibrations respectively [42,43]. The FT-IR spectra of PMA (Figure 3) shows an absorption band in the O-H stretching region at~3498 cm^{-1} have been assigned to the stretching vibrations originating from the O-H groups present in the Keggin structure of HPA. The absorption band at ~1614 cm^{-1}have been assigned to the bending vibrations of the O-H group belonging to the PMA.

SEM with EDX Analysis

The SEM-EDX pictures (magnification of 832X) of Ben and PMA-Ben are represented in (Figure 7 and Figure 8) respectively. The SEM pictures of Ben and PMA-Ben show no distinct change in the surface morphology and appears to have the layered structure. Therefore, it appears that the PMA is not adsorbed on the surface of the clay but is intercalated in the layers of the clay. This fact is also supported by the XRD and IR studies. The SEM results are also supported by the EDX analysis. In both the cases surface composition consist of Al, Si, O, Mg, Fe, Ca & K. No signal corresponding to P, Mo was supported by the EDX data which further shows that PMA may be in the interlayers region.

Characterization of Reaction Products

The aldehydes and ketones obtained during the reaction has been characterized using FT-IR and NMR

spectroscopy techniques.

- **Benzaldehyde:** IR (υ in cm^{-1}) 3065 (aromatic C-H), 1598,1584,1455 (aromatic ring), 1697 (C=O), 688 and 746 (mono. Subs.); ^{1}H NMR δ 10.1 (s,1H, CHO), 8.1 (d, 1H, H $_{6\ Aromatic}$), 7.9 (d, 1H, H $_{2\ Aromatic}$), 7.2-7.6 (m, 3H, H $_{3,4,5Aromatic}$).

- **4-Chloro Benzaldehyde:** IR (υ in cm^{-1}) 3087 (aromatic C-H), 1588,1573,1483 (aromatic ring), 1693 (C=O), 814 (p-Subs.); ^{1}H NMR δ 9.9 (s,1H, CHO), 7.9 (d, 2H, H $_{2,6\ Aromatic}$), 7.6 (d, 2H, H $_{3,5\ Aromatic}$).

- **2-Chloro Benzaldehyde:** IR (υ in cm^{-1}) 3100 (aromatic C-H), 1592,1568,1443 (aromatic ring), 1698 (C=O), 756 (o-Subs.); ^{1}H NMR δ 10.2 (s,1H, CHO), 7.6 (d, 1H, H $_{3\ Aromatic}$), 7.8 (d, 1H, H $_{6\ Aromatic}$), 7.4-7.5 (m, 2H, H $_{4,5\ Aromatic}$).

- **4-Hydroxy Benzaldehyde:** IR (υ in cm^{-1}) 3368 (aromatic O-H), 1598,1517,1453 (aromatic ring), 1667 (C=O), 1286 (C-O), 834 (p-Subs.); ^{1}H NMR δ 10.4 (s,1H, CHO), 9.6 (s, 1H, OH), 7.5 (d, 2H, H $_{3,5\ Aromatic}$), 6.7 (d, 2H, H $_{2,6\ Aromatic}$).

- **2-Hydroxy Benzaldehyde:** IR (υ in cm^{-1}) 3487 (aromatic O-H), 1581,1486,1460 (aromatic ring), 1666 (C=O), 1278 (C-O), 746 (o-Subs.); ^{1}H NMR δ 10.7 (s,1H, CHO), 10.2 (s, 1H, OH), 7.6 (d, 1H, H $_{3\ Aromatic}$), 7.4 (d, 1H, H $_{6\ Aromatic}$), 6.8-7.0 (m, 2H, H $_{4,5\ Aromatic}$).

- **4-Methoxy Benzaldehyde:** IR (υ in cm^{-1}) 3010 (aromatic C-H), 1579,1511,1461 (aromatic ring), 1685 (C=O), 1261 (C-O), 833 (p-Subs.); ^{1}H NMR δ 9.8 (s,1H, CHO), 7.8 (d, 2H, H $_{3,5\ Aromatic}$), 7.5 (d, 2H, H $_{2,6\ Aromatic}$), 3.8 (s, 3H,OCH$_3$).

- **2-Methoxy Benzaldehyde:** IR (υ in cm^{-1}) 3010 (aromatic C-H), 1578,1511,1461 (aromatic ring), 1683 (C=O), 1260 (C-O), 762 (o-Subs.); ^{1}H NMR δ 10.4 (s,1H, CHO), 8.0 (d, 1H, H $_{3\ Aromatic}$), 7.2-7.5 (m, 3H, H $_{4,5,6\ Aromatic}$), 2.2 (s, 3H, OCH$_3$).

- **Acetophenone:** IR (υ in cm^{-1}) 3063 (aromatic C-H), 1599,1583,1449 (aromatic ring), 1683 (C=O), 1266 (C-O), 760, 690 (monosubs.); ^{1}H NMR δ 7.9 (d, 2H, H $_{2,6\ Aromatic}$), 7.5 (m, 3H, H $_{3,4,5\ Aromatic}$), 2.2 (s, 3H, OCH$_3$).

- **4-Hydroxy Acetophenone:** IR (υ in cm^{-1}) 3309 (aromatic O-H), 1576,1511,1427 (aromatic ring), 1663 (C=O), 1280 (C-O), 848 (p-Subs.); ^{1}H NMR δ 10.2 (s,1H, OH), 7.9 (d, 2H, H $_{3,5\ Aromatic}$), 6.9 (d, 2H, H $_{2,6\ Aromatic}$), 2.6 (s, 3H, COCH$_3$).

- **2-Hydroxy Acetophenone:** IR (υ in cm^{-1}) 3350 (aromatic O-H), 1582,1487,1448 (aromatic ring), 1641 (C=O), 1244 (C-O), 755 (o-Subs.); ^{1}H NMR δ 10.2 (s,1H, OH), 7.7 (d, 1H, H $_{3\ Aromatic}$), 7.5 (d, 1H, H $_{6\ Aromatic}$), 6.8-6.9 (m, 2H, H $_{4,5\ aromatic}$), 2.6 (s, 3H, COCH$_3$).

REUSABILITY OF PMA-BEN FOR THE DEOXIMATION OF BENZALDEHYDE

The reusability of PMA-Ben has been investigated up to four repeated cycles using Deoximation of Benzaldehyde. The catalyst, PMA-Ben, was washed with MeOH after every cycle and was characterized using FT-IR, TGA, DSC, XRD, SEM and EDX etc. techniques. No noticeable changes were observed even after four cycles, which not only indicates the stability of the catalyst but also indicates that none of the reactants/products remain with the catalyst. The product/s, after separation and isolation, was characterized by the earlier described methods and the yield in each case was calculated (Figure 9). The variation in the yield was found to be in the range of ~ 94% to 85% of the theoretical yield.

The catalyst characterization was performed on the catalyst after the 4th cycle of reaction was performed on the catalyst and following observations was made.

- The SEM picture does not show any change in the surface morphology, the layered structure is maintained. The EDX data indicates the same elemental composition as earlier, i.e. Al, Si, O, Mg, Fe, Ca, K and Na. (Figure 10)

- The thermal stability of the catalyst was found to be unaffected after reuse except a slight change in the weight loss (from 11.7 % to 14%) which may be due to the presence of small quantity of adsorbed organic matter after the 4th cycle. (Figure 11)

- XRD and FTIR (Figure 12) data of PMA-Ben has been found to have no significant change as compared to the freshly synthesized PMA-Ben.

REFERENCES

1. T W Greene& P G M Wuts(1991) Protective Group in Organic Synthesis, 2nd ed**.** John Wiley andSons, New York 175.

2. R L Shriner,R C Fuson, D Y Curtin &T C Morrill (1980) The Systematic Identification of Organic Compounds, 6th ed.; Wiley: New York.

3. L G Donaruma&W Z Heldt (1960) Organic Reactions 11:1.

4. Sandler, S. R. & Karo, W. (1989) Organic Functional Group Preparation, Academic Press:San Diego, 430–481.

5. Kabalka, G.W., Wadgaonkar, P.P., & Pace, R. D. (1990).The Palladium Assisted Transfer Reduction of α, β-Unsaturated Nitroalkenes to Oximes Using Ammonium Formate. Synth Commun, 20,2453-2458

6. Quan, N., Shi, X.X., Nie, L.D., Dong, J., & Zhu, R.H. (2011).A Green Chemistry Method for the Regeneration of Carbonyl Compounds from Oximes by Using Cupric Chloride Dihydrate as a Recoverable Promoter for Hydrolysis. Synlett, 7, 1028-1032

7. Majireck, M.M., Witek, J.A., &Weinreb, S.M.(2010).An expedient reductive method for conversion of ketoximes to the corresponding carbonyl compounds. Tetrahedron Lett,51, 3555

8. Martin, M., Martinez, G., Urpi, F.,&Vilarrasa, J. (2004).Conversion of ketoximes to ketones with trimethylphosphine and 2,2′-dipyridyl diselenide. Tetrahedron Lett,45, 5559.

9. [9] Lukin, K. A., & Narayanan, B. A.(2002).The reaction of oximes with tributylphosphine–phenyldisulfide: mechanistic insight and new synthetic possibilities. Tetrahedron,58, 215-219

10. Curran, D. P., Brill, J. F., & Rakiewicz, D. M.(1984).A mild reductive conversion of oximes to ketones. J Org Chem,49, 1654-1656

11. Zhou, X. T., Yuan, Q. L., & Ji, H. B. (2010).Highly efficient aerobic oxidation of oximes to carbonyl compounds catalyzed by metalloporphyrins in the presence of benzaldehyde. Tetrahedron Lett,51, 613-617

12. Shaabani, A., & Farhangi, E.(2009). Cobalt(II) phthalocyanine catalyzed aerobic regeneration of carbonyl compounds from the corresponding oximes in 1-butyl-3-methylimidazolium bromide. Appl CatalA,371, 148-152

13. Ganguly, N. C., & Barik, S. K. (2008).A Facile, Catalytic Deoximation Method Using Potassium Bromide and Ammonium Heptamolybdate in the Presence of Hydrogen Peroxide in an Aqueous Medium. Synthesis, 425-428

14. Gupta, P. K., Manral, L., &Ganesan, K.(2007).An efficient approach for conversion of oxime into carbonyl compound using Dichloramine-T. Synthesis, 1930-1932

15. Gogoi, P., Hazarika, P., & Konwar, D. (2005). Surfactant/I₂/Water: An Efficient System for Deprotection of Oximes and Imines to Carbonyls under Neutral Conditions in Water. J Org Chem, 70, 1934-1936

16. Shaabani, A., Naderi, S., Rahmati, A., Badri, Z., Darvishi, M., &Lee, D. G.(2005). Cleavage of Oximes, Semicarbazones, and Phenylhydrazones with Supported Potassium Permanganate.Synthesis3023-3025

17. Khazaei, A.,& Manesh, A. A. (2005).Microwave-Assisted Chemoselective Cleavage of Oximes to Their Corresponding Carbonyl Compounds Using 1,3-Dichloro-5,5-dimethyl-hydantoin (DCDMH) as a New Deoximating Reagent. Synthesis,1929-1931

18. [18] Chavan, S. P.,&Soni, P.(2004).A facile deprotection of oximes using glyoxylic acid in an aqueous medium. Tetrahedron Lett,45, 3161-3162

19. Maynez, S. R., Pelavin, L.,&Erker, G.(1975).Regeneration of ketones from tosylhydrazones, arylhydrazones, and oximes by exchange with acetone. J Org Chem,40, 3302-3303

20. DePuy, C. H., &Ponder, B. W. (1959).Levulinic Acid as a Reagent for the Hydrolysis of Oximes and 2,4-Dinitrophenylhydrazones. J Am Chem Soc,81, 4629-4631

21. Luca, L. D., Giacomelli, G., &Porcheddu, A. (2002). Beckmann Rearrangement of Oximes under Very Mild Conditions.J Org Chem,67, 6272-6274

22. Gawley,R. E. (1988).Org React,35,1–420.

23. Barhate,N. B., Gajare, A. S., Wakharkar, R. D.,&Sudalai, A.(1997). Facile regeneration of carbonyl compounds from oximes and tosylhydrazones with TBHP. Tetrahedron Lett,38, 653-656

24. Rao, C. G., Radhakrishna, A. S., Singh, B. B., & Bhatnagar, S. P. (1983).Oxidative Cleavage of Oximes with Triethylammonium Chlorochromate. Synthesis, 808.

25. Drabowicz, J. (1980).Rapid Deoximation with Pyridinium Chlorochromate/Hydrogen Peroxide System. Synthesis,125-126

26. McKillop, A., Hunt, J. D., Naylor, R. D., &Taylor, E. C. (1971). Thallium in organic synthesis. XXVI. Direct conversion of oximes into aldehydes and ketones with thallium(III) nitrate (TTN).J AmChem Soc, 93, 4918-4919

27. Imanzadeh, G. H., Hajipour, A. R.,&Mallakpour, S. E.(2003). Solid State Cleavage of Oximes with Potassium Permanganate Supported on Alumina.Synth Commun, 33, 735-740

28. Khazaei, A., Manesh, A. A., & Ghasemi, A. H.(2004).Facile and Chemoselective Microwave-Assisted Cleavage of Oximes to Their Corresponding Carbonyl Compounds Using N,N'-Dibromo- N,N'-1,3-propylene-bis[(4-methylphenyl)sulfonamide] as a Deoximating ReagentSynthesis, 2784-2786

29. [Reddy, M. S., Narender, N.,&Rao, K. R. (2004). Regeneration of Carbonyl Compounds by Oxidative Cleavage of Oximes with NBS in the Presence of β-Cyclodextrin in Water.Synth Commun, 34, 3875-3881

30. De Lijser, H. J. P., Fardoun, F. H., Sawyer, J. R., & Quant, M. (2002). Photosensitized Regeneration of Carbonyl Compounds from Oximes. OrgLett, 4, 2325-2328

31. Imanzadeh, G. H., Zamanloo, M. R., Eskandari, H., & Banaei, A. R. (2006).Aqueous Media Deprotection of Ketoximes with Ammonium Persulfate. Bull Korean Chem Soc 27:119-120

32. Yang, Y., Zhang, D., Wu, L. Z., Chen, B., Zhang, L. P., & Tung, C. H. (2004).Photosensitized oxidative deprotection of oximes to their corresponding carbonyl compounds by platinum(II) terpyridyl acetylide complex. J Org Chem, 69, 4788

33. Shirini, F., Mamaghani, M.,&Rahmanzadeh, A. (2007).Efficient oxidative cleavage of C=N using chromium trioxide supported on $NaHSO_4.H_2O$. Arkivoc 34-39 Li, Z., Ding, R. B., Xing, Y. L., & Shi, S. Y. (2005). Solvent-Free Rapid Deprotection of Ketone and Aldehyde Oximes using Periodic AcidSynth Commun, 35, 2515-2520.

34. Choghamarani,G. A., Shiri, L.,&Zeinivand,J. (2008).Efficient, Catalytic and Oxidative Deoximation of Aldoximes and Ketoximes by Ferric Nitrate and Catalytic Amounts of Bromide Ion. J Bull Korean Chem Soc, 29, 2496-2498

35. Kim, B. R., Lee, H. G., Kim, E. J., Lee, S. G.,&Yoon, Y. J. (2010).Conversion of Oximes to Carbonyl Compounds with 2-Nitro-4,5-dichloropyridazin-3(2*H*)-one. J Org Chem, 75, 484-486

36. Salerno, P., Asenjo, M. B.,& Mendioroz, S. (2001). Influence of preparation method on thermal stability and acidity of Al–PILCs. Thermochimica acta, 379, 101.

37. Tyagi, B., Chudasama, C. D., Jasra, R. V. (2006). Characterization of surface acidity of an acid montmorillonite activated with hydrothermal, ultrasonic and microwave techniques.Appl Clay Science, 31, 16-28

38. Abd El-Wahab, M. M. M.,&Said, A. A. (2005).Phosphomolybdic acid supported on silica gel and promoted with alkali metal ions as catalysts for the esterification of acetic acid by ethanol. Journal of Molecular Catalysis A, 240, 109-118

39. Yildiz, N., Aktas, Z., &Calimli, A. (2004). Sulphuric Acid Activation of a Calcium Bentonite.Particulate Science and Technology, 22, 21-33

40. Temuujin, J., Jadambaa, T., Burmaa, G., Erdenechimeg, Sh., &Amarsanaa, J. (2004).Characterisation of acid activated montmorillonite clay from Tuulant (Mongolia). Ceramics International, 30, 251-255

41. Araujo, E. M., Melo, T. J. A., Santana, L. N. L., Neves, G. A., Ferreira, H. C., Lira, H. L., Carvalho, L. H., Avila Jr, M. M., Ponte, M. K. G.,&Araujo, I. S.(2004). The influence of organo-bentonite clay on the processing and mechanical properties of nylon 6 and polystyrene composites. Materials SciEng B,112, 175-178

42. Valverde JL, Canizares P, Kou MRS, Molina CB(2000). Enhanced Thermal Stability of Al-Pillared Smectites Modified with Ce and La.Clays and Clay Minerals, 48, 424-432

APPENDICES

Table 1: Optimization of Catalyst Amount

S. No.	Catalyst (mg)	Time, Sec	%Yield of Benzaldehyde with Various Catalysts					
			Ben	Al-Ben$_2$	H$^+$-Ben	PAAC-Ben$_2$	PMA	PMA-Ben
1	20	60	30	42	45	52	50	67
2	30	60	40	50	52	60	58	75
3	40	60	52	60	63	70	67	82
4	**50**	60	57	70	73	80	78	**94**
5	60	60	58	70	73	80	78	94

Table 2: Optimization of Time

S. No.	Time, Sec.	Yield, %
01	20	70
02	30	83
03	40	90
04	50	92
05	60	94
06	70	94

Table 3: Product Synthesized
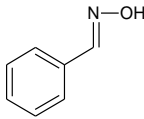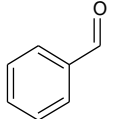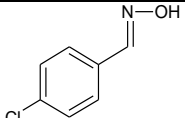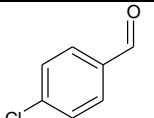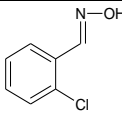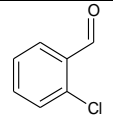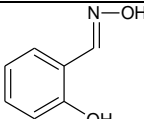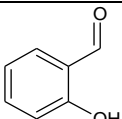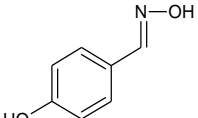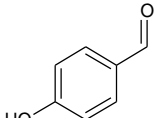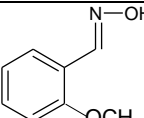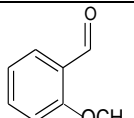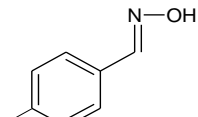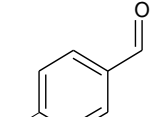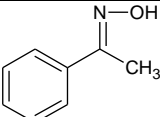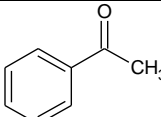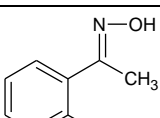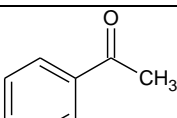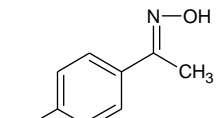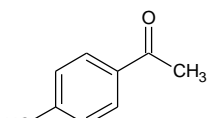
S. No.	Reactant	Product	Time, Sec	Yield, %	Remarks
01			60	94	Single product
02			80	90	Single product
03			80	87	Single product
04			40	97	Single product
05			40	97	Single product
06			40	98	Single product
07			40	98	Single product
08			70	90	Single product
09			60	92	Single product
10			60	93	Single product

Table 4: Surface Area

Catalysts	Total Surface Area, (m^2/g)
Ben	215.0
Na-Ben	121.3
Al-Ben	295.2
H$^+$-Ben	327.2
PAAC-Ben	350.1
PMA-Ben	296.0
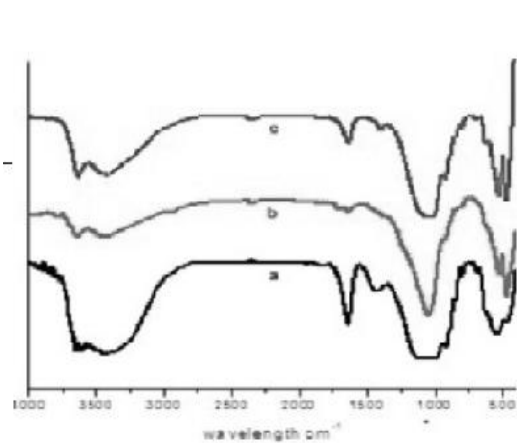
Figure 1: FTIR Spectra of (a) Ben, (b) Na-Ben, (c)H$^+$-Ben
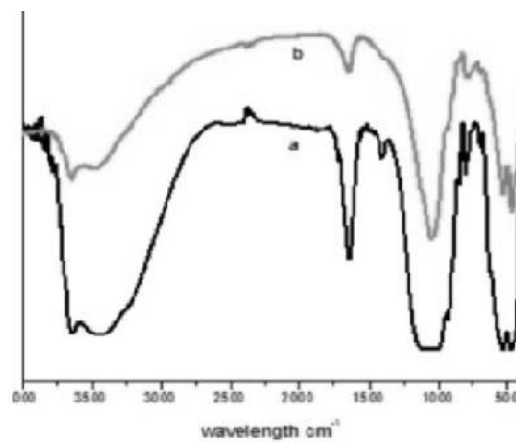
Figure 2: FTIR Spectra of (a) Al-Ben, (b) PAA-Ben
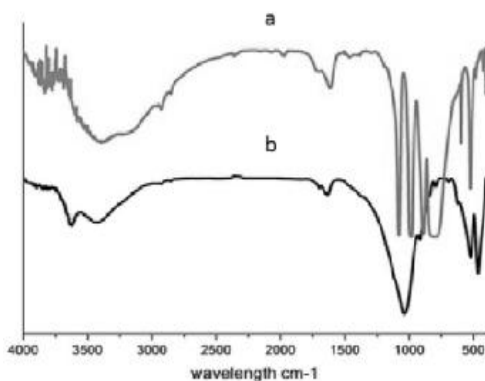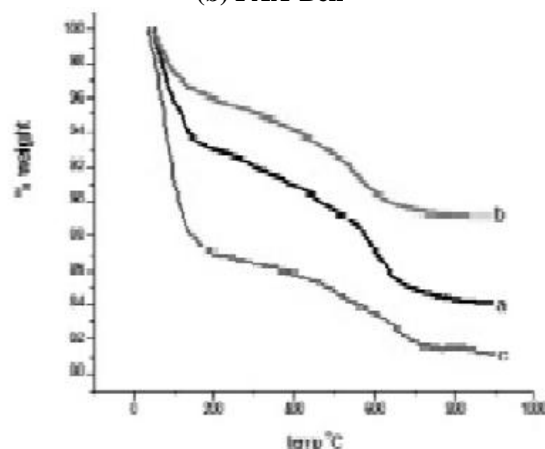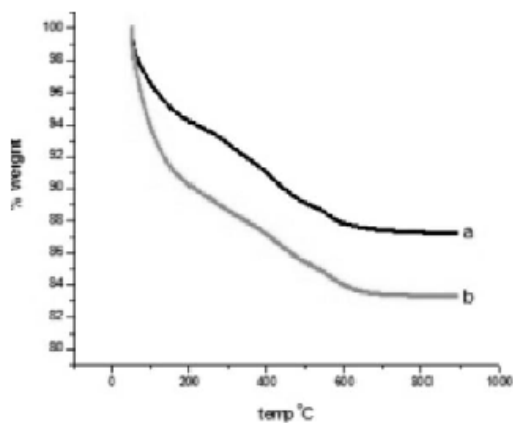

Figure 3: FTIR Spectra of (a) PMA, (b) PMA-Ben

Figure 4: TGA Studies of (a) Ben, (b) Na-Ben, (c)H$^+$-Ben

Figure 5: TGA Studies of (a) Al-Ben, (b) PAA-Ben
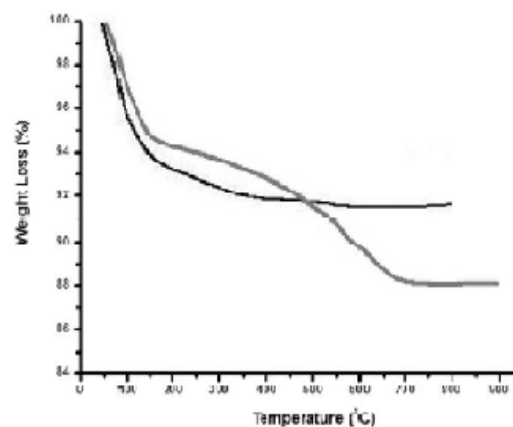
Figure 6: FTIR Spectra of (a) PMA, (b) PMA Ben
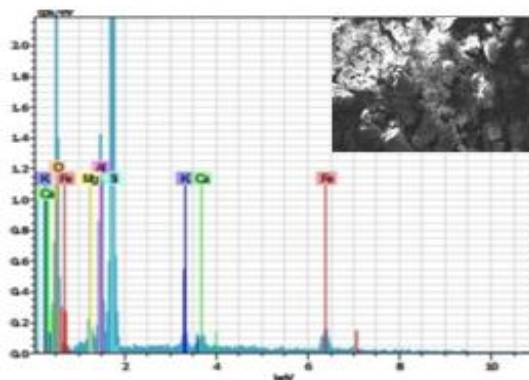
Figure 7: SEM-EDX of Ben
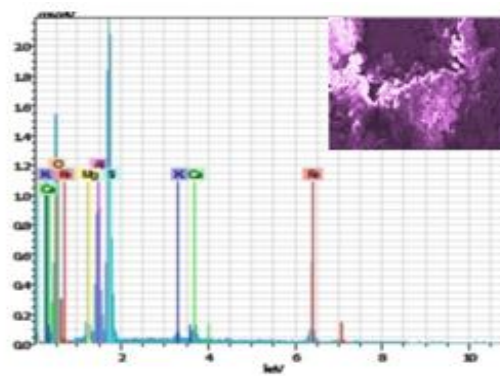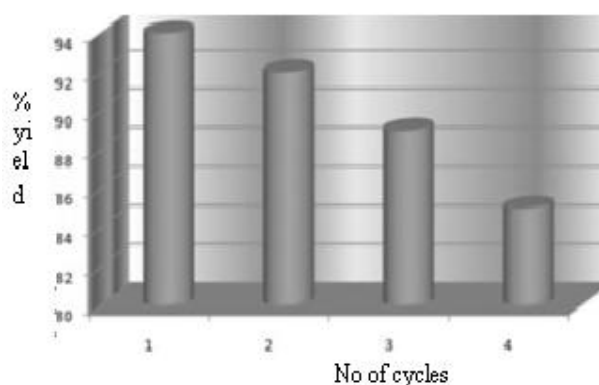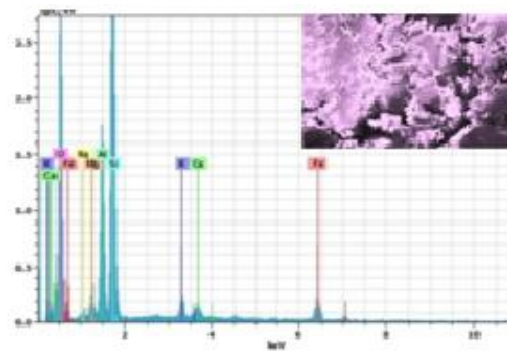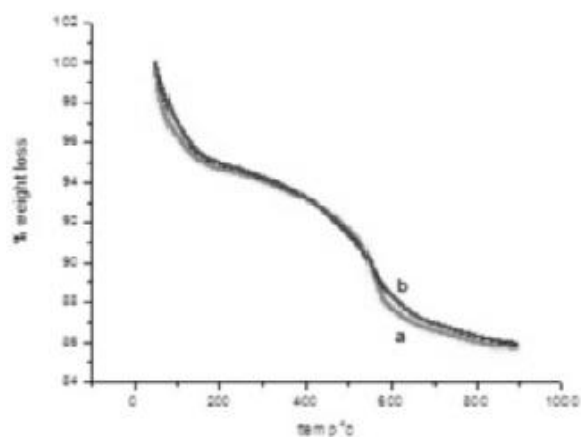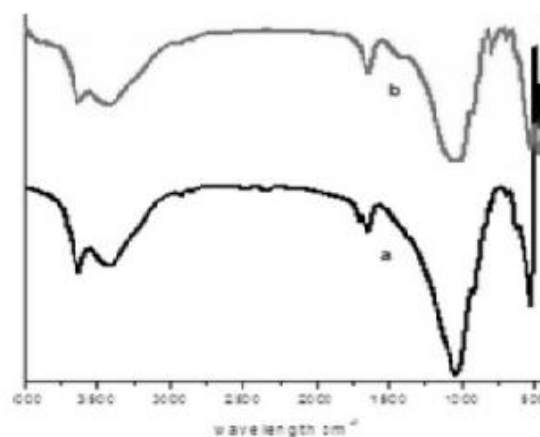

Figure 8: SEM-EDX of PMA-Ben

Figure 9: Reusability of PMA-Ben up to 6 Repeated Cycles

Figure 10: SEM and EDX of PMA-Ben after 6th Cycle

Figure 11: TGA Studies of (a) PMA-Ben after 1st Cycle (b) PMA-Ben after 6th Cycle

Figure 12: FTIR Spectra of (a) PMT-Ben after 1st Cycle, (b) PMA-Ben after 6th Cycle